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Nanomedicine & Nanotechnology Open Access
ISSN: 2574-187X

The Characterization and Application of a Prepared Photo-Catalytic TiO_2 Coating on Glazed Ceramic Tiles

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Research Article

Volume 2 Issue 3

Received Date: August 29, 2017

Published Date: September 05, 2017

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Abstract

Photocatalytic TiO_2 coating was synthesized on glazed ceramic tiles by suitable thermal treatment. The structural and morphological properties were investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The photocatalytic effect was investigated in fighting against fungal and bacterial growth under sunlight irradiation for the purpose of manufacturing ceramic tiles that are fungal and bacterial resistant to be used in the lining of water treatment storage reservoirs and swimming pools.

Keywords: Photocatalysis; Titanium oxide; Sol–gel; Glazed ceramic tiles

Introduction

In the recent years, scaling optical and electronic properties of nanomaterials focused attention on the preparation of nanoparticle semi-conductors [1]. Well-dispersed titania nanoparticles with very fine sizes are promising in many applications such as pigments, adsorbents and catalytic supports [2-4]. In almost all of these cases, when the particle size is reduced greatly to nano scales, some novel optical properties are expected [5]. Photocatalysis is a promising technology for the purification of pre-treated and non-biodegradable waste water [6]. Photocatalysts have been widely used for the decomposition of harmful compounds in environment [7]. Among different photocatalytic materials, titania (TiO_2) is the most attractive material due to its unique properties like high chemical stability, non-environmental impact, and low cost [8]. So, TiO_2 is being used in different applications such as disinfection and detoxification of water and waste water, air purification, anti-fogging surfaces, self-cleaning surfaces, self-sterilizing surfaces, amongst other applications [8-10]. TiO_2 is an effective material for the degradation of dyes from waste water [11-13]. Titanium dioxide exists in both crystalline and amorphous forms and mainly exists in three crystalline polymorphos, namely, anatase, rutile and brookite. Anatase and rutilehave a tetragonal structure, whereas brookite has an orthorhombic structure [14]. The immobilization of TiO_2 nanoparticles on an appropriate support has been widely accepted since it could help to eliminate the costly phase separation processes and to promote the practicality of such catalysts as an industrial process. The photocatalytic activity of immobilized TiO_2 particles on macroporous ceramic alumina foams has been reported [15].

It was found that reticulated macroporous ceramic foam with an open three-dimensional structure assure low flow resistance and improves light penetration and fluid flow. This offers a promising support for photocatalytic applications and water purification systems. TiO_2 thin films have found application in dye-sensitized solar cells (DSSC) because of their interconnected pore networks and large surface area, which allows sufficient dye adsorption and efficient light harvesting. Hence, the performance of such cells depends on the nature of porous structure and average particle size [16-21].

The aim of this paper is to synthesize TiO_2 nanoparticles and coatings applied on the surface of glazed ceramic tiles by using a sol–gel method. Anatase is the most widely used photocatalytic agent because of its high photocatalytic activity, non-toxicity and durability. Native solar energy can be used as a clean energy source to inhibit surface growth of fungi and bacteria on lining materials used in storage water reservoirs. White ware is a generic term for ceramic products which are usually white and of fine texture. Glazing is important in white wares. A glaze is a thin coating of glass melted onto the surface of porous ceramic ware. It contains ingredients of two distinct types in different proportions: i) refractory materials such as feldspar, silica and china clay, ii) fluxes such as soda, potash, fluorspar and borax. Nephelinesyenite permits firing at a lower temperature. The glaze may be put on by dipping, spraying, pouring, or brushing [22]. Once the raw materials are processed, a number of steps take place to obtain the finished product. These steps include batching, mixing and grinding, spray-drying, forming, drying, glazing, and firing. Many of these steps are now accomplished using automated equipment.

Materials and Methods

Preparation of TiO_2 nanoparticles

TiO_2 nanoparticles were prepared by sol-gel method [23]. In a typical method, 4ml of titanium (IV) isopropoxide was added to 80 ml bi-distilled water during vigorous stirring. Then 5 ml of acetic acid and 0.4ml of nitric acid were added during continuous stirring of the sol at constant heating at 80°C for 4-5 hours.

Immobilization of TiO_2 nanoparticles on silica gel (TiO_2/SiO_2) was done by adding appropriate amounts of silica gel powder during sol-gel formation process. The complete sol containing the silica gel was then transferred to a Teflon-lined autoclave and heated for 12 h at 190°C. The obtained gel was then dried at 80°C till complete evaporation of the solvent and the obtained powder was then calcined at 450°C for 30 min.

Preparation of Tio_2 Coating on Ceramic Tiles

The percentage oxide composition of glaze used was as follows: Al_2O_3 (8.79%), SiO_2(62.23%), B_2O_3 (5.55%), CaO (8.98%), MgO (1.82%), ZnO (2.51%), K_2O (3.70%), Na_2O (0.81%) and ZrO_2 (5.61%). TiO_2 was added into glazed ceramic tiles by means of spraying technology using a small spray gun. The quantity of deposition was estimated to be about 1.2 g transparent sol per cm^2.

Photo Degradation Experiments

Ceramic tiles coated by TiO_2 were tested for micro-organisms growth by fixing on the walls of water reservoirs in Basyoun Water and Sanitation Company drinking water treatment plant. Reservoirs of water under coagulation process were used. The coated tiles were studied over periods of time up to 4 months in areas exposed to direct sunlight.

Identification of Algae

Algae were identified on ceramic surfaces by the usual morphological examination using a light microscope.

Identification of Bacteria

Gram staining is a bacteriological laboratory technique [24]. Bacteria on two ceramic tiles were examined by culturing on nutrient agar for 24 hours at 37°C.

Results and Discussion

The XRD analysis of the prepared sample of TiO_2 nanoparticles was done using a APD 2000 pro x-ray Diffractometer, wavelength (λ)=1.5406 Å and data was taken for the 2 Ɵ range of 10° to 70° with a step of 0.1972°. The results confirmed the nano sized powder TiO_2.

The X-ray diffraction pattern of the synthesized Titania nanoparticles is shown in Fig.1 reports that absence of spurious diffractions indicates the crystallographic purity. The 2Ɵ at peak 25.4° confirms the TiO_2 anatase structure [25]. Strong diffraction peaks at 25° and 48° indicating TiO_2 in the anatase phase [26-28]. The 2Ɵ peaks at 25.27° and 48.01° confirm its anatase structure. The intensity of XRD peaks of the sample reflects that the formed nanoparticles are crystalline and broad diffraction peaks indicate very small size crystallite.

The crystalline sizes of powder samples were based on the main peak calculated using the well-known Scherrer equation

$$A=\frac{K\lambda}{\beta cos\theta}$$

where K is the shape factor (here, K=0.89), λ is the wave length of the X ray beam used (λ=0.15405 nm), θ is the Bragg angle, and β is the full width at half maximum (FWHM) of the X ray diffraction peak. The average crystallite size of a-TiO_2 is only 3.4 nm.

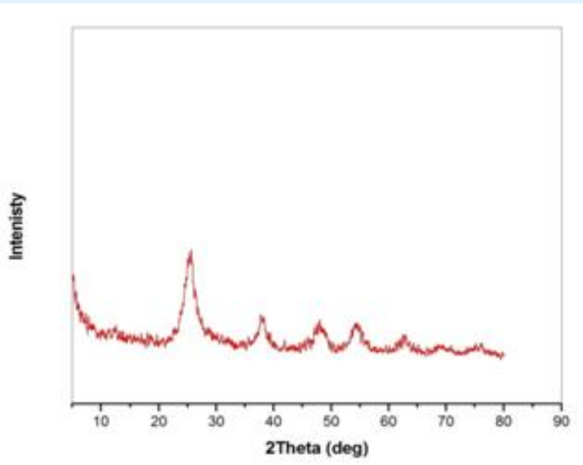


Figure 1: XRD spectra of TiO_2 nanoparticles.

In order to obtain the morphology of the TiO_2powder, SEM observation was carried out. Fig. 1 shows the SEM image of the dried gel and TiO_2powder. The grains are nearly spherical with approximately uniform particle size and its distribution ranging between 3 and 100nm, which are clearly observed in Figure 1.

The scanning electron microscopic (model: JEOL JSM 6510 LV) images for as- prepared TiO_2 nanoparticlesis shown in Figure 2. The SEM surface images of TiO_2 coating heat-treated at 1100°C. It is seen that there is a smooth surface at low magnification is shown in Figure 3.

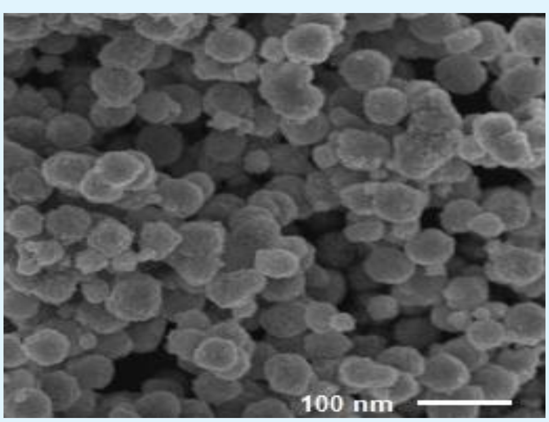


Figure 2: SEM images for as- prepared TiO_2 nanoparticles.

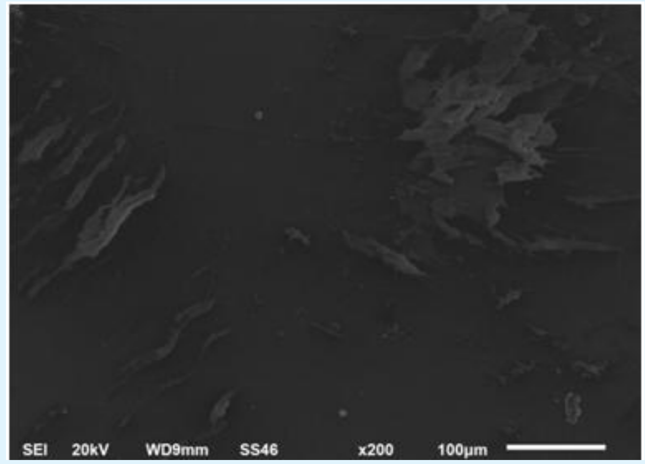


Figure 3: SEM surface images of TiO_2 coating.

The SEM (model: JEOL JSM 6510 LV) cross-section image of a TiO_2 coated glazed tile is shown in Figure 4 a,b. Three layers are seen including the ceramic tile body, the glaze and the TiO_2 coating layer. The thickness of the a-TiO_2 coating is 343nm, which is tightly integrated with the glaze layer (Figure 4 a,b). In addition, EDS (EDS, model Oxford X-Max 20) was used to quantitatively determine the elemental composition. The EDS spectra of TiO_2 coating reveals that the TiO_2 coating is mainly composed of Ti and O elements is shown in Figure 4c. The mass percent of Ti element is 20.35 wt%, while that of O is 43.58 wt%.

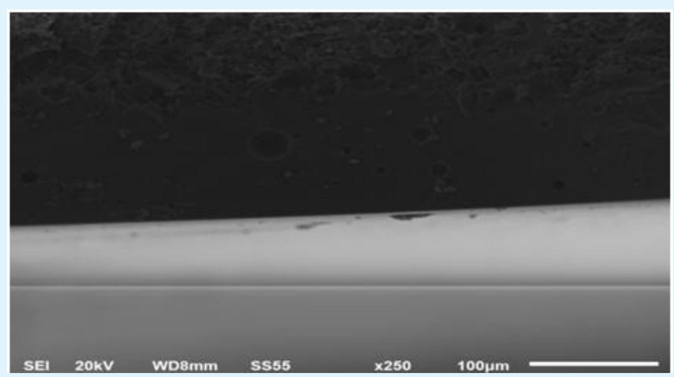


Figure 4a: SEM cross-section images of TiO_2–coated glazed tile.

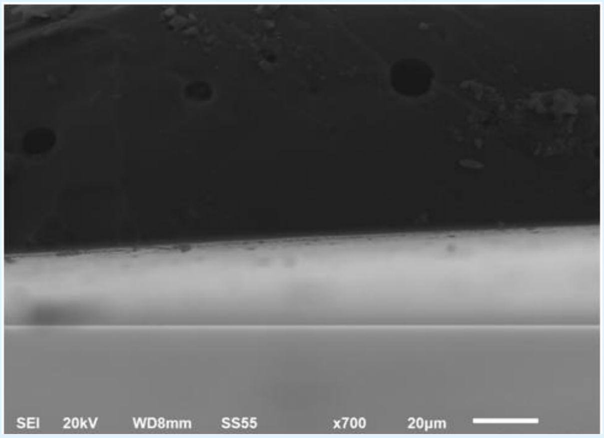


Figure 4b: SEM cross-section images of TiO_2–coated glazed tile.

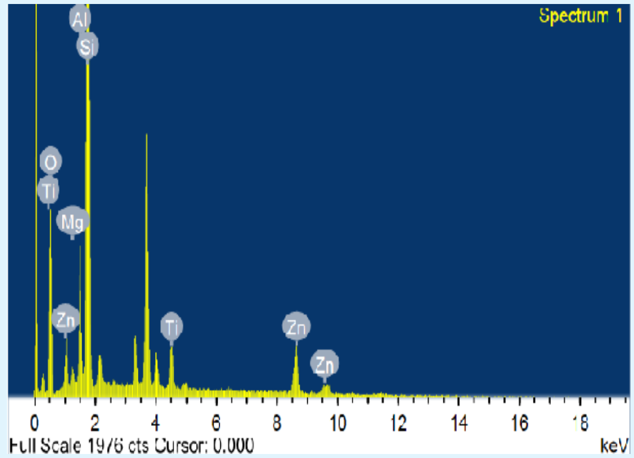


Figure 4c: EDS spectrum of TiO_2 – coated glazed tile.

The visual appearance of micro-organisms progressing growth on the surface of TiO_2 uncoated and coated tiles under sunlight irradiation is shown in Table 1. The study was extended for four months. Table 1 shows Comparison between micro-organisms progressing growth on the surfaces of TiO_2 uncoated and coated tiles under sunlight irradiation.

Period	Uncoated with TiO2	Coated with TiO2
After 10 days		
After one month		
After two month		

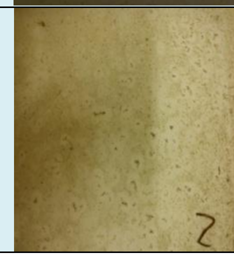
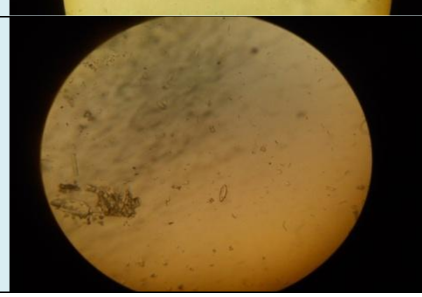
After three month		
After four month		

Table 1: Comparison between micro-organisms progressing growth on the surfaces of TiO_2 uncoated and coated tiles under sunlight irradiation.

Results in Table 1 reveals that the photocatalytic activity of TiO_2 plays a remarkable role in the inhibition of micro-organisms growth on glazed tile surfaces. This is due to the fact that when TiO_2 is illuminated with the lightof λ < 390 nm, electrons are promoted from the valence band to the conduction band of the semiconducting oxide to give electron-hole pairs. The valence band (h^+_{VB}) potential is positive enough to generate hydroxyl radicals at the surface and the conduction band (e^-_{CB}) potential is negative enough to reduce molecular oxygen. The hydroxyl radical is a powerful oxidizing agent of pollutants present at or near the surface of TiO_2.

Identification of algae on the un-coated glazed ceramic tiles was performed according to usual morphological criteria showing the growth of Spirogyra, Diatoms, Chlorella and mougeotiais shown in Table 2. Upon using TiO_2-coated glazed ceramic tile, only Chlorella algae growth was morphologically identified is shown in Figure 4. Table 2 shows identification of algae on the un-coated glazed ceramic tiles was performed according to usual morphological criteria.

spirogyra	
diatoms	

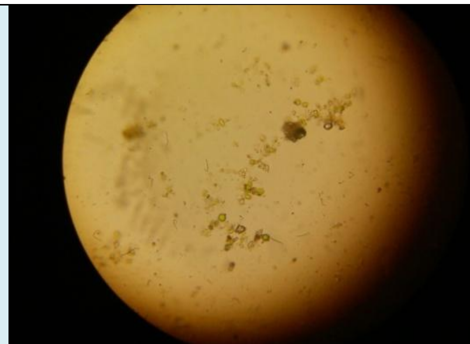
chlorella	
mougeotia	

Table 2: Identification of algae according to usual morphological criteria.

Chlorella algae growth was morphologically identified upon using TiO_2-coated glazed ceramic tile under sunlight irradiation is shown in Figure 5.

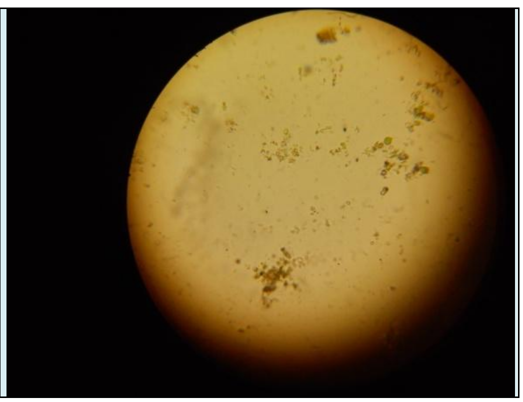
Chlorella	

Figure 5: Morphological identification of Chlorella algae growth upon using TiO_2-coated glazed ceramic tile under sunlight irradiation.

The total coliform bacteria test is negative for both ceramic tile coating with TiO_2 and non coating with TiO_2.

The apparent bacterial growth behavior is also different upon taking cultures from TiO_2 uncoated and coated tiles under sunlight irradiation is shown in Figure 6, bacteria identification showing existence ofgram positive cocci on TiO_2 coated tiles and existence of gram positive cocci and diplococci on TiO_2 uncoated tiles is shown in Table 3.

Ceramic with TiO_2	Ceramic without TiO_2
Gram positive Cocci	Gram positive Cocci and diplococci

Table 3: Show bacteria identification on two tiles.

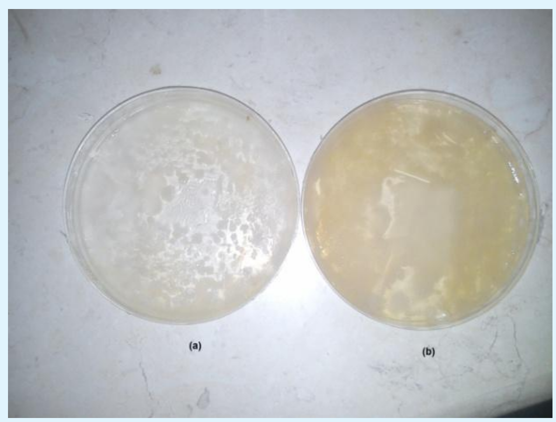


Figure 6: Bacterial growth on nutrient agar for cultures taken from tile surfaces of TiO_2- treated (a) and untreated (b) glazed tiles.

Identification of fungi on ceramic tiles according to the usual morphological criteria under light microscope both of ceramic tiles with TiO_2 and without TiO_2 not contain fungi is shown in Table 4.

Ceramic with TiO_2	Ceramic without TiO_2
-ve	-ve

Table 4: Show identification of fungi on both ceramic.

Conclusion

Titanium dioxide (TiO_2) nanoparticles have been successfully synthesized using a sol-gel method. The size and morphology of the samples were characterized using scanning electron microscopy (SEM). TiO_2 coated on glazed ceramic tiles to fight against micro-organisms growth in water storage reservoirs and swimming pools. Therefore, the ceramic tiles coated TiO_2 may be applied in lining of these installations allowing the use of sunlight as a clean and environmentally – friendly energy source. The application of TiO_2 coating enables minimizing the frequently exhausting and environmentally hazardous cleaning- up process of these installations.

Competing Interests

The authors declare that there is no conflict of interest regarding the publication of this paper.

Acknowledgements

This work is supported by ceramica prima factory at El Sadat City Fifth Industrial Zone, Egypt.

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